

# Modelling of a fluidized bed carbonator reactor to capture CO<sub>2</sub> from a combustion flue gas

Alonso M<sup>1\*</sup>; Rodríguez N<sup>1</sup>; Grasa G<sup>2</sup>; Abanades J.C.<sup>1</sup>

<sup>1</sup>Instituto Nacional del Carbón, CSIC, Francisco Pintado Fe, 26 Oviedo 33011, Spain

<sup>2</sup>Instituto de Carboquímica, CSIC, Zaragoza 50015, Spain

## Abstract

In recent years several processes incorporating a carbonation-calcination loop in an interconnected fluidized bed reactor have been proposed as a way to capture CO<sub>2</sub> from flue gases. This paper is a first approximation to the modelling of a fluidized bed carbonator reactor. In this reactor the flue gas comes into contact with an active bed composed of particles with very different activities, depending on their residence time in the bed and in the carbonation-calcination loop. The model combines the residence time distribution functions with existing knowledge about sorbent deactivation rates and sorbent reactivity. The fluid dynamics of the solids (CSTR) and gases (PF) in the carbonator are based on simple assumptions. The carbonation rates are modelled defining a characteristic time for the transition between a fast reaction regime to a regime with a zero reaction rate. On the basis of these assumptions the model is able to predict the CO<sub>2</sub> capture efficiency for the flue gas depending on the operating and

---

\* Ph: 34-985119090 Fax: 34-985297662 E-mail: mac@incar.csic.es

design conditions. Operating windows with high capture efficiencies are discussed, as well as those conditions where only modest capture efficiencies are possible.

**Keywords:** Chemical reactors, design, energy, environment, mathematical modelling, CO<sub>2</sub> capture

## Introduction

The UN Intergovernmental Panel for Climate Change (IPCC), Nobel Prize laureate for Peace in 2007, has already established that CO<sub>2</sub> capture and storage “*would be an option in the portfolio of actions for stabilization of greenhouse gas concentrations while allowing for the continued use of fossil fuels*” (Metz et al. 2005 ). Large scale “capture systems” are already operating in the gas, oil and chemical industries, where CO<sub>2</sub> and other key gases (H<sub>2</sub> or O<sub>2</sub>) are routinely separated from different process streams. Such existing technologies could be adapted for the capture of CO<sub>2</sub> in flue gases from fossil fuel power plants at an acceptable cost (30-50 \$/t CO<sub>2</sub> avoided) compared to other methods of large scale power production with near-zero CO<sub>2</sub> emissions. Despite the maturity of several of these existing capture systems, it is widely recognized that there is need for large reductions in the CO<sub>2</sub> capture costs and energy efficiency penalties. Indeed lower costs and lower energy penalties are currently the driving forces behind all R&D in this emerging area.

One promising means of CO<sub>2</sub> capture for coal based power plants is to use a lime carbonation-calcination cycle (or “carbonate looping”) which is illustrated in Figure 1. This process was originally proposed by Shimizu et al. 1999, and uses CaO as a

regenerable sorbent to capture  $\text{CO}_2$  from combustion flue gases. Other processes that use CaO in combustion systems have been proposed (Wang et al. 2004; Abanades et al. 2005) while others have also been considered for  $\text{H}_2$  production routes (Yi and Harrison 2005; Ochoa-Fernandez et al. 2007; Pfeifer et al. 2007; Sun et al. 2007; Weimer et al. 2008).

In the basic system of Fig. 1  $\text{CO}_2$  is captured from the combustion flue gas of a power plant in a circulating fluidized bed carbonator operating between 600-700°C. When the solids leave the carbonator (with some of the CaO being converted to  $\text{CaCO}_3$ ) they are directed to a second fluidized bed where calcination/regeneration takes place. Coal burns in the calciner in an atmosphere of  $\text{O}_2/\text{CO}_2$  at temperatures over 900°C, thus producing the heat necessary to calcine the  $\text{CaCO}_3$  back to CaO and  $\text{CO}_2$ . It is assumed that this second fluidized bed calciner operates with oxygen supplied by an air separation unit, but other sources of heat for calcination may be used in the future (Abanades et al. 2005). The  $\text{CO}_2$  captured from the flue gases as  $\text{CaCO}_3$ , and the  $\text{CO}_2$  produced by the oxy-fired combustion of coal in the calciner, are recovered in concentrated form from the calciner gas, which is now suitable for final purification and compression, and subsequently for transport and safe storage in a deep geological formation. The calciner employs a considerable fraction (35-50%) of the total energy entering the system to heat the incoming gas and solid streams up to the calciner temperatures and in order to provide the heat necessary for the endothermic calcination of  $\text{CaCO}_3$  (Rodriguez et al. 2008). However this energy leaves the system in mass streams at high temperature (at  $T > 900^\circ\text{C}$ ) or is recovered as carbonation heat in the carbonator (at around 650°C). Thus the large energy input into the calciner comes out of the system as high quality heat that can be recycled in a highly efficient steam cycle

(Shimizu et al. 1999; Abanades et al. 2005; Romeo et al. 2008). The calciner functions in fact like a new oxyfired fluidized bed power plant. But in this new power plant it may be possible to almost double the amount of CO<sub>2</sub> output thanks to the CO<sub>2</sub> captured in the carbonator as CaCO<sub>3</sub> and regenerated back to CaO and CO<sub>2</sub> in the oxyfired calciner.

The carbonator reactor depicted on the left hand side of Figure 1 is therefore a key process unit that must be designed and operated in such a way as to achieve high capture efficiencies of CO<sub>2</sub> from the flue gas. The flow rates of flue gases from a typical 1000 MWt power plant are about 300 Nm<sup>3</sup>/s. Bringing this huge flow of gas into contact with CaO particles is only possible with reactors of a very high gas throughput per unit area such as circulating fluidised bed reactors. In addition, we may take advantage of the mechanical similarities between the carbonator and the currently employed large scale circulating fluidised bed combustors that operate with gas velocities, solid circulation rates and types of solid similar to those required to implement the carbonation-calcination loop.

Despite the increasing number of published works that deal with different aspects of such systems (sorbent performance and reactivation studies, batch experiments and modelling, process simulation work etc) there is a lack of information about the role of the fluidized bed carbonator reactor in systems such as that depicted in Figure 1. The purpose of this study is to fill this knowledge gap by proposing a model based on simple assumptions about the fluid-dynamics of the reactors involved and by integrating existing knowledge about sorbent capture capacity and reactivity to the residence time distribution functions of the particles cycling between the carbonator and calciner reactors in the loop of Figure 1. The results of this work will help to gain insight into the

operating modes of these reactors when they are employed at large scale. They may also be helpful for designing of pilot plants in which the process can be tested in continuous mode or for interpreting the results obtained from small pilot plants (10-70 kW thermal) like those entering operation in Canada, Germany, Spain, France and the UK under the C3 Capture project of the EU and other projects.

## Model Description

As mentioned above, the main objective of the model is to estimate CO<sub>2</sub> capture efficiency,  $E_{carb}$ , in the carbonator, where:

$$E_{carb} = \frac{CO_2 \text{ reacting with CaO in the bed}}{CO_2 \text{ entering the bed in the flue gas}} \quad (1)$$

The overall mass balances in the system can be written as:

$$\left( \begin{array}{c} CO_2 \text{ reacting with} \\ CaO \text{ in the bed} \end{array} \right) = \left( \begin{array}{c} CO_2 \text{ removed from} \\ the \text{ gas phase} \end{array} \right) = \left( \begin{array}{c} CaCO_3 \text{ formed in the} \\ circulating \text{ stream of CaO} \end{array} \right) \quad (2)$$

The model is solved when all the terms in the previous equation have been calculated for a given set of input operating and design conditions. The first assumptions that need to be made to set up equations for the different terms concerned: the instantaneous and perfect mixing of solids in the carbonator and in the calciner, the plug flow for the gas phase in the carbonator, and the instantaneous and complete calcination of the particles in the calciner.

It can be seen from the notation in Figure 1 that the flue gas entering the carbonator reactor contains a feed of CO<sub>2</sub> ( $F_{CO_2}$  in mol CO<sub>2</sub>/s), which will disappear through the carbonation reaction of the CaO active particles present in the bed. The bed contains  $N_{Ca}$  mol of Ca but only a fraction of the CaO,  $f_a$ , reacts in the bed at a rate  $r_{ave}$  (average

reaction rate of the active material,  $s^{-1}$ ). The remaining fraction of bed particles ( $1-f_a$ ) are considered inactive, as will be explained below. At the same time, there is a continuous arrival of new calcined particles ( $F_R$ ) that are converted in the perfectly mixed carbonator reactor to a carbonation conversion  $X$ :

$$\left( \begin{array}{l} CO_2 \text{ removed from} \\ \text{the gas phase} \end{array} \right) = F_{CO_2} \times E_{carb} \quad (3)$$

$$\left( \begin{array}{l} CaCO_3 \text{ formed in the} \\ \text{circulating stream of CaO} \end{array} \right) = F_R \times X \quad (4)$$

$$\left( \begin{array}{l} CO_2 \text{ reacting with} \\ \text{the CaO bed} \end{array} \right) = N_{Ca} \times f_a \times r_{ave} \quad (5)$$

The concept of  $f_a$  was already introduced in a previous work modelling batch carbonation experiments (Abanades et al. 2004). To explain the meaning of  $f_a$  in this work we must first review what is known about the reaction mechanism and reaction rates of the carbonation reaction. It is well known that the carbonation reaction has a fast reaction regime followed by a slow reaction regime controlled by  $CO_2$  diffusion through the product layer of  $CaCO_3$  formed on the free  $CaO$  surfaces (Deadman and Owens 1962; Bhatia and Perlmutter 1983; Mess et al. 1999). Furthermore, it is also well established that the maximum conversion of  $CaO$  (that marks the end of the fast carbonation period) decreases rapidly as the number of carbonation calcinations cycles increases (Curran et al. 1967; Barker 1973; Abanades and Alvarez 2003; Grasa and Abanades 2006). In order to model these key sorbent features, and to facilitate the integration of the rate and the residence time distributions it is assumed that the  $CaO$  particles attain the maximum conversion,  $X_N$ , at a constant rate, in a characteristic time  $t^*$ , and after that the reaction rate becomes zero.

$$r_{CaO} = \begin{cases} \frac{X_N}{t^*} & \text{if } t < t^* \\ 0 & \text{for } t > t^* \end{cases} \quad (6)$$

Figure 2 illustrates this reaction model. For illustrative purposes, several series of experimental data from Grasa et al. 2008 are also included. More elaborate models for the kinetics of the carbonation reaction are likely to appear in the future, but we believe the model of equation 6 is sufficient at this stage as long as the characteristic  $t^*$  is consistent with the experimental measurements. This equation implies that particles with a residence time higher than  $t^*$ , reach their maximum average conversion,  $X_N$ , and that their reaction rate is zero from that point onwards. Particles with a residence time lower than  $t^*$  approach their maximum conversion at a reaction rate that is constant for a given cycle number. As will be shown below, setting the rate of reaction and the fraction of active particles of the bed as functions of  $t^*$  greatly facilitates the resolution of the model.

The maximum conversion,  $X_N$  in equation 6 is the conversion that the particles reach at the end of the fast carbonation period, which depends on the number of calcination-carbonation cycles in accordance with the following equation (Grasa and Abanades 2006):

$$X_N = \frac{1}{\frac{1}{(1-X_r)^{Nk}} + 1} + X_r \quad (7)$$

where typical values of  $k = 0.52$  and  $X_r = 0.075$  (Grasa and Abanades 2006). Therefore, equation 6 allows the calculation of the rate of carbonation of a particle that is progressing towards its maximum allowable carbonation conversion  $X_N$ , given by equation 7 as a function of the number of cycles,  $N$ . However, with the continuous feed

of fresh particles and the purging of solids from the perfectly mixed beds of Figure 1, there will be a large population of particles in the system with different cycle numbers, different capacities for CO<sub>2</sub> capture (depending on N) and different reactivities (also depending on N). Particle size did not influence the sorption capacity of the sorbent that remains determined only by the number of calcination/carbonation cycles (N) (Grasa and Abanades 2006).

The mass balance to estimate the fraction of particles that have been cycling in the system N times was solved in a previous work (Abanades 2002) for a carbonation-calcination loop with full maximum carbonation conversion (represented by eq. 7) and total calcination. This mass balance may be refined for conditions where these reactions are incomplete, but for the sake of simplicity it is retained here.

The average maximum carbonation conversion that can be achieved by the particles in the carbonator is the average of the individual conversions:

$$X_{ave} = \sum_{N=1}^{N=\infty} r_N X_N \quad (8)$$

where (see ref. (Abanades 2002)):

$$r_N = \frac{F_0 F_R^{N-1}}{(F_0 + F_R)^N} \quad (9)$$

Taking into account the kinetic model for an individual particle represented by equation (6), and assuming that the solids are perfectly mixed, it is possible to calculate the average reactivity of the CaO particle in the bed,  $r_{ave}$ , by replacing the subscript “N” in equation 6 by the subscript “ave” as calculated in equation 8. This means that equations 6-9 allow the calculation of the rate at which the bed is capturing CO<sub>2</sub> (equation 5)



when the average concentration of CO<sub>2</sub> and the inventory of active calcium particles in the bed are known ( $N_{Ca} \times f_a$ ). As will be shown below, the most important variable to be taken into account when estimating the average concentration of CO<sub>2</sub> in the bed is also the fraction of active particles that is reacting in the fast reaction regime,  $f_a$ .

As shown in Figure 2, the fraction of active particles,  $f_a$ , corresponds to the particles that have not yet fully reached their maximum possible conversion or, in other words,  $f_a$  is the fraction of particles with a residence time in the carbonator below  $t^*$ . Therefore, for a perfect mixed model,  $f_a$  is defined as:

$$f_a = \left(1 - e^{-t^*/\tau}\right) \quad (10)$$

where  $\tau$  is the average particle residence time in the carbonator which is defined as:

$$\tau = \frac{N_{Ca}}{F_R} = \frac{W_{CaO}}{56F_R} \quad (11)$$

Thus taking into account the simple reaction model adopted in Figure 2, it can be seen that the CaCO<sub>3</sub> leaving the carbonator reactor is the sum of two contributions: carbonate in particles converted to their maximum level of conversion (with a residence time higher than  $t^*$ ) depending on their individual cycle number, and particles with a residence time lower than  $t^*$ , which abandon the carbonator when they are still reacting at the rate given by equation 6:

$$\left( \begin{array}{l} \text{CaCO}_3 \text{ formed} \\ \text{in the circulating stream of CaO} \end{array} \right) = F_R X = F_R \left( f_a X|_{<t^*} + (1 - f_a) X|_{>t^*} \right) \quad (12)$$

The conversion of particles when  $t > t^*$  is:

$$X|_{>t^*} = X_{ave} \quad (13)$$

Since  $r_{ave}$  is constant between 0 and  $t^*$ ,  $X|_{<t^*}$  can be calculated as follows:

$$X|_{t^*} = \frac{\int_0^{t^*} (r_{ave} \times t) \frac{1}{\tau} e^{-t/\tau} dt}{f_a} = r_{ave} \tau \frac{\left[ 1 - e^{-t^*/\tau} \left( \frac{t^*}{\tau} + 1 \right) \right]}{(1 - e^{-t^*/\tau})} \quad (14)$$

Using equation 12 for  $r_{ave}$ , and incorporating equation 13 and 14 into equation 12, the following expression for the average carbonate conversion of the solids leaving the carbonator reactor is obtained:

$$X = X_{ave} \frac{\tau}{t^*} (1 - e^{-t^*/\tau}) \quad (15)$$

or substituting equation 13 to express X in terms of  $f_a$ :

$$X = X_{ave} \frac{f_a}{\ln(1/(1 - f_a))} \quad (16)$$

The difference between the maximum conversion achievable by the solids in the carbonator,  $X_{ave}$ , and the actual conversion of the solids leaving the reactor, X, represents the fraction of CaO that was originally active in the calcined solid stream entering the carbonator and that has not yet been converted to  $\text{CaCO}_3$ . The difference between this fraction of active CaO, defined as  $(X_{ave} - X)$ , and the fraction of active CaO,  $f_a$ , defined previously as the fraction of CaO particles reacting in the fast reaction regime (i.e. with residence times lower than  $t^*$ ) is worth noting. Because of the simple kinetic model adopted (constant carbonation rate from  $t=0$  to  $t=t^*$  irrespective of conversion) the fraction  $f_a$  contains a certain fraction of  $\text{CaCO}_3$  (given by equation 14), and therefore  $f_a > (X_{ave} - X)$ .

Substituting the result of eq. 16 into eq. 4:

$$\left( \frac{\text{CaCO}_3 \text{ formed in the}}{\text{circulating stream of CaO}} \right) = F_R X = F_R X_{ave} \frac{f_a}{\ln(1/(1 - f_a))} \quad (17)$$

so that the carbonation efficiency in the carbonator reactor can be defined as a simple function of  $f_a$ :

$$E_{carb} = \frac{F_R}{F_{CO_2}} X_{ave} \frac{f_a}{\ln(1/(1-f_a))} \quad (18)$$

As stated in equation 2, the carbon balance in the reactor demands identical carbonation efficiency to account for the disappearance of  $CO_2$  from the gas phase and to account for the reaction of  $CO_2$  with the active CaO in the bed (also depending of  $f_a$  according to equation 5). For a given set of input data  $F_R$ ,  $F_0$ ,  $F_{CO_2}$ ,  $W_{CaO}$  (or  $N_{Ca}$ ), and for a given sorbent defined by its deactivation and reactivity constants, there is only one value of  $f_a$  that provides an identical value of  $E_{carb}$  when this is calculated from equation 18 or from equation 5. Therefore, in order to close the mass balance and solve the model, we need to develop equation 5 to find an equation for the reaction rate,  $r_{ave}$ , as a function of process conditions.

The first step is to define a rate expression for the carbonation reaction of the solids entering the carbonator consistent with the kinetic model adopted in previous paragraphs and represented in Figure 2. In accordance with equation 8 the calcined particles of CaO are entering the carbonator with a maximum capacity to carbonate up to  $X_{ave}$ . It has also been established in a previous work (Alvarez and Abanades 2005) that for most limestones and cycle numbers, the maximum conversion of a particle is attained when there is a carbonate layer of 50 nm thickness on the pore wall (Alvarez and Abanades 2005). So, the specific reaction surface at the beginning of the N cycle,  $S_N$ , and the maximum conversion  $X_N$  can be related as follows:

$$X_N = \frac{e_{max} S_N \frac{\rho_{CaCO_3}}{PM_{CaCO_3}}}{\frac{\rho_{CaO}}{PM_{CaO}}} \quad (19)$$

Equation 19 allows the estimation of the average reaction surface available for the CaO particles entering the carbonator as:

$$S_{ave} = \frac{X_{ave} \frac{\rho_{CaO}}{PM_{CaO}}}{e_{max} \frac{\rho_{CaCO3}}{PM_{CaCO3}}} \quad (20)$$

Once reaction surface has been calculated and assuming kinetic control in the reaction of CaO with CO<sub>2</sub> during the fast reaction regime:

$$r_{ave} = k_s S_{ave} (C_{CO2} - C_{e,CO2}) \quad (21)$$

This rate expression is similar to the one used in previous works (Abanades et al. 2004; Grasa and Abanades 2006), but without the term  $(1-X)^{2/3}$ , which is characteristic of grain models. This modification is a minor one in quantitative terms, considering that conversions are typically low except in the first few cycles and that there will be few particles of this type in the continuous process of Figure 1 (see below). Bhatia and Perlmutter 1983 also used a similar first order expression and found that the intrinsic carbonation rate constant was around  $5.95 \cdot 10^{-10} \text{ m}^4 (\text{mol s})^{-1}$ . The rate constant for highly cycled particles has recently been determined by Grasa and Abanades 2006 and it is consistently within a range of  $3.2 \cdot 10^{-10}$  to  $8.9 \cdot 10^{-10} \text{ m}^4 (\text{mol s})^{-1}$ . Unless stated otherwise, in this work we adopt a conservative value of  $4 \cdot 10^{-10} \text{ m}^4 (\text{mol s})^{-1}$ .

With the rate of reaction of the active particles in the bed defined by equation 21, it is possible to formulate the carbon mass balance in the gas phase in a differential element of the carbonator reactor. Assuming that the gas passes in plug flow through a bed of perfectly mixed solids, the balance for a differential element is:

$$F_{CO_2} \frac{dE_{carb}}{dz} = A f_a \frac{\rho_{CaO}}{PM_{CaO}} r_{ave} = A \cdot f_a \cdot \frac{\rho_{CaO}}{PM_{CaO}} \cdot k_S \cdot S_{ave} \cdot \rho_{M,g} \left[ \frac{(f_0 - f_e) + (f_0 f_e - f_0) E_{carb}}{(1 - f_0 E_{carb})} \right] \quad (22)$$

Using a dimensionless variable for height, the integrated form of this equation is:

$$\frac{F_{CO_2} \cdot PM_{CaO}}{W_{CaO} \cdot k_S \cdot S_{ave} \cdot \rho_{M,g} \cdot f_a} \left[ \frac{-f_0}{(f_0 f_e - f_0)} E_{carb} + \frac{f_0 (f_0 - 1)}{(f_0 f_e - f_0)^2} \ln \left( \frac{(f_0 - f_e) + (f_0 f_e - f_0) E_{carb}}{(f_0 - f_e)} \right) \right] = z' \quad (23)$$

where the equilibrium molar fraction of CO<sub>2</sub> is calculated from the expression (Barker 1973):

$$f_e = \frac{10^{(7.079 - \frac{8308}{T})}}{P_{total}} \quad (24)$$

where T is the operation temperature (K) and P the total system pressure (atm).

By means of this implicit equation, it is possible to determine the CO<sub>2</sub> concentration profile along the carbonator when z' takes values between 0 and 1. At the exit of the carbonator (z'=1), the carbonation efficiency calculated from eq. 23 needs to be equal to the carbonation efficiency calculated from eq. 18. In fact, the model is solved when there is a solution of f<sub>a</sub> that yields identical carbonation efficiencies in the gas and solid material balances.

A matlab code was developed to solve the model and the sequence of calculations used by the program is shown in Figure 3 and briefly outlined here.

There is a set of input conditions (F<sub>R</sub>, F<sub>0</sub>, F<sub>CO<sub>2</sub></sub>, W<sub>CaO</sub>) and a set of constant values characteristic of the sorbent (k<sub>S</sub>, k, X<sub>r</sub>). The average activity of the sorbent, or the maximum allowable conversions, X<sub>ave</sub>, can be calculated using eq. 8. Although there are simpler expressions for X<sub>N</sub> that allow an analytical solution of this infinite sum

(Abanades 2002), this is not possible if equation 7 is used, and therefore the summing of equation 8 is carried out numerically with sufficient cycle numbers (N) as to guarantee that the sum of the volume fractions given by equation 9 is higher than 0.99.

Assuming from this point the presence of a volumetric fraction of active CaO in the bed,  $f_a$ , the carbonation efficiency is calculated by two parallel routes, iterating the value of  $f_a$  until both routes yield the same efficiency (allowing for an error of 1%). Whereas the first calculation route uses equation 18, the second route uses the same  $f_a$ . In this case the carbonation efficiency is calculated at the carbonator exit ( $z'=1$ ) and solving for the implicit equation 23.

Finally, to facilitate the Discussion section that follows, we must define an average  $\text{CO}_2$  concentration in the gas phase, that will allow an estimation of the average reaction rate from equation 21 which, when applied to equation 5, will also yield the overall carbonation efficiency. This is similar to the concept of the mean logarithmic concentration widely used in plug flow reactors. In this case, from the design equations for a CSTR and a PFR assuming a first order of kinetic reaction:

$$k\tau = \frac{\rho_{M,g} f_0 E_{carb}}{(f_{CO2} - f_e)} \quad (25)$$

$$k\tau = \frac{E_{carb}}{\int_0^1 \frac{f_0 \rho_{M,g} (1 - f_0 x) dX}{[(f_0 - f_e) + (f_0 f_e - f_0) X]}} \quad (26)$$

Solving the integral and making both equations equal, we get:

$$(f_{CO2} - f_e) = \frac{E_{carb}}{\left[ -\frac{f_0}{(f_0 f_e - f_0)} E_{carb} + \left( \frac{(f_0 f_e - f_0) + (f_0 - f_e) f_0}{(f_0 f_e - f_0)^2} \right) \ln \left( \frac{(f_0 - f_e) + (f_0 f_e - f_0) E_{carb}}{(f_0 f_e - f_0)^2} \right) \right]} \quad (27)$$

Applying this average concentration to the bed, the average reactivity of the active particles in the bed ( $f_a$ ) is:

$$r_{ave} = \frac{\rho_{CaO} k_s S_{ave} \rho_{M,g} (\overline{f_{CO_2}} - f_e)}{PM_{CaO}} \quad (28)$$

Applying this equation with  $N_{Ca}$  and the solution of  $f_a$  from the model yields the same capture efficiency as the one obtained from eq. 18 or 23.

## Discussion

The model has been applied to conditions representative of a real case (a power plant delivering a given flow rate of  $CO_2$ ,  $F_{CO_2}$ , in the flue gases fed to the capture system via the carbonator). The objective of the model is to achieve a reasonable estimate of the capture efficiency. The model described in the previous paragraphs is able to calculate this efficiency when the different parameters in equations 2, 4 and 5 can be estimated from the operating conditions and the sorbent deactivation and reactivity parameters can be obtained from the laboratory experiments. As in the case of any fluidized bed reactor (Kunii and Levenspiel 1990; Levenspiel 2005) there is a need for a good knowledge of the fluid-dynamics of the circulating fluidized bed carbonator to determine the solid circulation rate ( $F_R$ ) the inventory of  $CaO$  in the riser ( $W_{CaO}$ ) and the gas-solid contact quality. However, it is beyond the scope of this work to incorporate a fluidynamic submodel to the carbonator reactor model. Instead, we will show that the carbonator reactor can operate at a reasonable set of values for the key fluidynamic variables ( $F_R$  and  $W_{CaO}$ ) in circulating fluidized bed systems. What might be considered “reasonable” for a new process like the one being considered in this work is open to discussion, but it is clear that the process will be more credible and ready for scaling up if the typical

values of the solid circulation rates and solid inventories are within the range of values characteristic of similar systems such as circulating fluidized bed combustors, CFBC. Assuming that this is the case, the mechanical design of the twin reactor system in Figure 1 and the choice of sorbent particle size distribution and operation conditions (surface gas velocities in the risers) should be such as to ensure the circulation of solids between the reactors ( $F_R$ ) and the presence of solids inventory in the carbonator reactor ( $N_{Ca}$  or  $W_{CaO}$ ) which, according to the model, is necessary to achieve a high  $CO_2$  capture efficiency. CFBC power plants can operate with solid circulation rates between 1-45 kg/m<sup>2</sup>s, whereas solids inventories could in principle range from a few thousand Pa to the 0.02-0.03 MPa characteristic of dense bubbling fluidized beds. High solids inventories in a fluidized bed reactor increase the residence time of the circulating solids and maximise their conversion but, at the same time, they cause a high pressure drop that in turn leads to a higher power consumption by fans.

In the following paragraphs we will use the model to discuss the performance of the carbonator reactor over a wide range of reasonable values for the key operating parameters  $F_R$  and  $W_{CaO}$ . The choice of parameters to solve the model was justified in the description of the model. All the calculations shown below are expressed by MWt calculated for a typical coal combustion power plant (0.15 volumetric fraction of  $CO_2$  and 0.1 kg  $CO_2$ /s). To translate the results to per m<sup>2</sup> of crosssectional area of the carbonator, one has to bear in mind that a typical heat duty in a commercial CFBC is around 5MWt/m<sup>2</sup>.

Figure 4 shows the  $CO_2$  capture efficiency as a function of the solids inventory ( $W_{CaO}$ ) at different  $F_R/F_{CO_2}$  ratios and for two different  $F_0/F_{CO_2}$  ratios. The interval chosen for



$F_R/F_{CO_2}$  (between 1 and 20) is consistent with CaO solid circulation rates between 0.6 kg/m<sup>2</sup>s and 12.3 kg/m<sup>2</sup>s. Two values of  $F_0/F_{CO_2}$  were chosen to illustrate the impact of the make up flow of fresh limestone on the system (around 0.5 kg of limestone per kg of coal when  $F_0/F_{CO_2}$  is 0.1 as in Figure 4a, and around 0.05 kg/kg of coal when this is 0.01 as in Figure 4.b). Both figures show that CO<sub>2</sub> capture efficiency rises rapidly for low values of  $W_{CaO}$  until it reaches asymptotically a certain limit. It can be seen that there is an upper limit for all the curves representing the equilibrium (a thick dotted horizontal line in each Figure). The predicted CO<sub>2</sub> capture efficiencies approach this equilibrium limit when the flow of active CaO ( $F_R \cdot X_{ave}$ ) is higher than the flow of CO<sub>2</sub>,  $F_{CO_2}$ , and there is a sufficient bed inventory to ensure that most CaO particles entering the carbonator in  $F_R$  reach a conversion close to their maximum (given by equation 8). When this is not the case and  $F_R \cdot X_{ave} < F_{CO_2}$ , the carbonation capacity of the solids entering the carbonator is not sufficient to capture all the CO<sub>2</sub> being fed into the carbonator. Hence, the CO<sub>2</sub> carbonation efficiency is limited by the  $F_R/F_{CO_2}$  ratio. Again, the upper limit of efficiency (indicated by thin dashed lines in Figure 4) is only reached when the solids inventory is sufficiently high to ensure that most of the solids achieve their maximum carbonation conversion. In view of this, one might be inclined to favour system operation modes with the highest possible solid circulation rates,  $F_R$ . However, as  $F_R$  increases, the solids inventory required to achieve a certain level of solid conversion also increases (so that the same solids residence time is maintained). Furthermore, the heat balance between the calciner and carbonator also imposes certain limits: since it is important to minimize the heat requirements in the calciner it is necessary to reduce the heat required to heat up the solids circulating from the carbonator to the calciner at a lower temperature. This makes it necessary to operate the

system with moderate solid circulation rates, ideally no higher than 20 kgCaO/m<sup>2</sup>s (Rodriguez et al. 2008).

The effect of  $F_0/F_{CO_2}$  on the predicted CO<sub>2</sub> capture efficiencies in Figure 4 b can also be explained by similar arguments. When the make up flow of fresh limestone is low, the average activity,  $X_{ave}$ , of the solids arriving at the carbonator is low (it would equal  $X_r$  for  $F_0/F_{CO_2} = 0$ ). The low value of  $X_{ave}$  would require higher values of solid circulation,  $F_R$  between the reactors, for  $F_R * X_{ave}$  to match the value of  $F_{CO_2}$ . Figure 5 plots the effect of the  $F_0/F_{CO_2}$  ratio on CO<sub>2</sub> capture efficiency for two examples of  $F_R/F_{CO_2}$  ratios of 20 and 5 and two examples of solid inventories of 50 kg/Mw and 200 kg/Mw. Theoretically, when there is no make up flow of fresh limestone, there is no loss of sorbent in the system and the average activity of the sorbent particles in stationary state is the residual activity given by equation 7,  $X_{ave} = X_r$ . In these conditions, the maximum CO<sub>2</sub> capture efficiency for very large values of  $W_{CaO}$  is only proportional to the solid circulation rate. Thus it may be possible to attain capture efficiencies close to 90% with no make up flow of sorbent, given sufficiently large solid inventories (over 200 kg/MW) and sufficiently large solid circulating rates (higher than 12 kgCaO/m<sup>2</sup>s). Of course this is a theoretical limit that cannot be attained in practice because the losses of sorbent from attrition and the need to purge solids to extract ashes and CaSO<sub>4</sub>, require a continuous make up flow of fresh limestone. However, despite the strong deactivation of CaO with respect to the carbonation reaction after several carbonation-calcination cycles (equation 7), it is theoretically feasible to compensate for the low residual capture capacity by using a higher solid circulation rate, which is within the limits acceptable for similar CFBC units. As can be seen in Figure 5, high capture efficiencies are also possible for a much wider range of solid circulation rates and solids inventories when

there is a make up flow of fresh limestone that improves the average activity or carbonation capacity of the material circulating between the reactors. It should also be noted that for a low  $F_R/F_{CO_2}$ ,  $CO_2$  capture efficiency is more sensitive to changes in the  $F_0/F_{CO_2}$  ratio for both solids inventories. This is not surprising considering that for moderate and low solid circulation rates, only highly active solids (a high  $X_{ave}$  due to a high  $F_0/F_{CO_2}$ ) can achieve high levels of capture efficiency. Figure 5 shows that there is a range of design choices to be made in order to attain high solid capture efficiencies. The model proposed will be a valuable tool for understanding the trade off between high capture efficiency and minimizing the make up flow of fresh limestone, while at the same time maintaining reasonable solid circulation rates and a sufficient solids inventory in the carbonator.

The  $CO_2$  concentration profiles in the carbonator are also a function of  $F_R/F_{CO_2}$  and  $F_0/F_{CO_2}$  and the average activity of the sorbent (equation 23). Figure 6 exemplifies the  $CO_2$  volume fraction axial profiles in the carbonator for different situations. Assuming that the gas in the carbonator reactor is in plug flow, the bed height can be normalized between 0 and 1 for any crosssection of the bed. The equilibrium limit is again represented by a dotted line. Three types of characteristic curves represent the situations already discussed in the previous paragraphs for  $CO_2$  capture efficiency. In Figure 6, the make up flow of limestone is 0.02 kg/s and the average activity of the sorbent circulating in the system is 0.32, 0.17, 0.11, for the three  $F_R/F_{CO_2}$  chosen. There is a sharp drop in  $CO_2$  concentration in the bed in the case of the high solid circulation rate, because of the low carbonation conversion achieved by the sorbent arriving from the calciner. Consequently, the fraction of active solids in the bed ( $f_a$ ) is higher (equation 16). In these conditions, the first quarter of the bed is sufficient to absorb most of the

CO<sub>2</sub> fed into the reactor. Although this scenario yields very high capture efficiencies, it should be avoided in practice because most of the bed is not effectively capturing CO<sub>2</sub> and therefore, there is an unnecessarily high value of solid circulation rates and solids inventories. In contrast there is a curve corresponding to a very low value of solid circulation rates ( $F_R/F_{CO_2} = 1$ ) that yields a CO<sub>2</sub> concentration profile associated to a low capture efficiency at the exit of the reactor ( $E_{carb} = 0.32$ ). The residence time of the solids is 20 times higher than in the previous case, and they achieve a conversion very close to their maximum at these conditions ( $X_{ave} = 0.32$ ). However it leads to a very ineffective bed (which is full of deactivated CaO and CaCO<sub>3</sub>) where few particles are reacting with the gas ( $f_a = 0.022$ ). The scenario that offers the optimum combination of conditions is the one represented by the curve for  $F_R/F_{CO_2} = 5$ . The CO<sub>2</sub> capture efficiency is sufficiently large (in this case  $E_{carb}=0.78$ ) and this is achieved with a reasonably low value of solid circulation rates, bed inventory and make up flow ratio.

All the calculations discussed in the previous paragraphs have been performed assuming that there is no other resistance to the progress of the carbonation reaction than the kinetic reaction. This assumption has been confirmed by recent kinetic studies on the carbonation reaction (Grasa and Abanades 2006) which show that the typically large pores present in deactivated particles of CaO do not introduce a relevant resistance to the progress of the reaction for typical particle size ranges in CFBs (70-400 micron). However, any deviation from the ideal plug flow model adopted for the gas phase or any other mechanism of deactivation of the CaO surface (e.g partial sulfation) may reduce the carbonation rates represented by equation 21. For this reason, we carried out a sensitivity analysis to estimate the impact of a reduction of the rate parameter on the predicted carbonation efficiencies. The results are represented in Figure 7 for an

effective kinetic constant 5 and 10 times lower than the intrinsic kinetic constant for typical  $F_0/F_{CO_2}$  and  $F_R/F_{CO_2}$  ratios (0.1 and 10 respectively). As expected, a reduction in the rate of reaction causes a substantial drop in the  $CO_2$  capture efficiencies when the other parameters are kept constant. If the sorbent shows a lower reactivity towards carbonation,  $CO_2$  capture efficiency decreases sharply, in particular for the lower range of solids inventories, when the solid residence times are lower and their conversion is mainly limited by the rate of the carbonation reaction. In contrast, the predicted capture efficiency tends to converge to the same value at high values of bed inventory, because with sufficiently large solids residence times, all particles would achieve their maximum carbonation conversions given by equation (8).

## Conclusions

The results obtained with the model presented in this work show that given a wide range of reasonable conditions for solid circulation rates, solids inventory and typical CaO reactivity parameters, a high  $CO_2$  capture efficiency can be expected from a carbonate looping system when it is applied to combustion flue gases. The model also reveals many conditions in which the capture of  $CO_2$  from the flue gas cannot be effective. This may be due to an insufficient solid circulation rate or solids inventory or to insufficient sorbent activity. The proposed model is based on very simple assumptions about the fluid dynamics of the gas (plug flow) and solids (instant and perfect mixing), but it can integrate in a transparent way the information available about sorbent reactivity and deactivation during cycling.  $CO_2$  capture efficiencies of over 80% are feasible when bed inventories are higher than 200 kg/Mw and solid circulation rates are higher than 3 kg/m<sup>2</sup>s for a typical reaction performance of CaO particles from natural sorbents and

make up flows of around 0.5 kg of limestone per kg of coal. Moreover capture efficiencies of over 90% are achievable in a wide range of conditions when solid circulation rates are increased (up to 6 kg/m<sup>2</sup>s). Thus the model presented in this work may serve as a valuable tool for designing and optimizing postcombustion carbonate looping systems.

### **Acknowledgements**

Alonso M. and Rodriguez N. acknowledge the grants received from the JAE-Doc Program from CSIC and FICYT.

## Notation

$E_{\text{carb}}$ , CO<sub>2</sub> capture efficiency in the carbonator.

$F_{\text{CO}_2}$ , CO<sub>2</sub> molar flow rate at the inlet of the carbonator, mol s<sup>-1</sup>.

$N_{\text{Ca}}$ , mol of Ca in the carbonator including CaO and CaCO<sub>3</sub>, mol.

$f_a$ , volumetric fraction of CaO that reacts in the carbonator in the fast reaction regime.

$r_{\text{ave}}$ , average reaction rate of the active material, s<sup>-1</sup>.

$X_N$ , maximum conversion of particles in the N cycle.

$F_R$ , molar flow rate of CaO coming from the calciner, mol s<sup>-1</sup>.

$X$ , solid conversion at the exit of the carbonator.

$t^*$ , characteristic time at which the reaction rate becomes zero, s.

$X_{\text{ave}}$ , maximum average conversion of solids.

$r_N$  particle fraction in the N cycle.

$F_0$  molar flow rate of fresh limestone, mol s<sup>-1</sup>.

$\tau$ , average residence time in the carbonator, s.

$W_{\text{CaO}}$ , solid inventory in the carbonator, kg.

$X|_{<t^*}$  conversion of particles with a residence time lower than  $t^*$ .

$X|_{>t^*}$  conversion of particles with a residence time higher than  $t^*$ .

$S_N$ , reaction surface in the N cycle (m<sup>-1</sup>).

$e_{\text{max}}$ , maximum thickness of the layer of CaCO<sub>3</sub> on the pore wall (50 nm).

$\rho_{\text{CaCO}_3}$ , CaCO<sub>3</sub> density, gm<sup>-3</sup>.

$\rho_{\text{CaO}}$  CaO density, gm<sup>-3</sup>.

$PM_{\text{CaCO}_3}$ , molecular weight of CaCO<sub>3</sub>, gmol<sup>-1</sup>.

$PM_{\text{CaO}}$ , molecular weight of CaO, gmol<sup>-1</sup>.

$k_s$ , kinetic constant, m<sup>4</sup>(mol s)<sup>-1</sup>.

$C_{\text{CO}_2}$  inlet concentration of CO<sub>2</sub>, mol m<sup>-3</sup>.

$C_{\text{CO}_2,e}$  the  $\text{CO}_2$  equilibrium concentration at reaction conditions,  $\text{mol m}^{-3}$ .

$z$ , carbonator height, m.

$A$  carbonator section,  $\text{m}^2$ .

$S_{\text{ave}}$  maximum average reaction surface,  $\text{m}^{-1}$ .

$\rho_{\text{M,g}}$  molar density of the gas,  $\text{mol m}^{-3}$ .

$f_0$ , inlet molar fraction of  $\text{CO}_2$ .

$f_e$ , molar fraction of  $\text{CO}_2$  at the point of equilibrium in the reaction conditions.



## References

- Abanades, J. C. (2002). The maximum capture efficiency of CO<sub>2</sub> using a carbonation/calcination cycle of CaO/CaCO<sub>3</sub>. *Chemical Engineering Journal*, 90: 303-306.
- Abanades, J. C., Alvarez, D. (2003). Conversion limits in the reaction of CO<sub>2</sub> with lime. *Energy & Fuels*, 17: 308-315.
- Abanades, J. C., Anthony, E. J., Lu, D. Y., Salvador, C., Alvarez, D. (2004). Capture of CO<sub>2</sub> from combustion gases in a fluidized bed of CaO. *AIChE Journal*, 50: 1614-1622.
- Abanades, J. C., Anthony, E. J., Wang, J. S., Oakey, J. E. (2005). Fluidized bed combustion systems integrating CO<sub>2</sub> capture with CaO. *Environmental Science & Technology*, 39: 2861-2866.
- Alvarez, D., Abanades, J. C. (2005). Determination of the critical product layer thickness in the reaction of CaO with CO<sub>2</sub>. *Industrial & Engineering Chemistry Research*, 44: 5608-5615.
- Barker, R. (1973). Reversibility of the reaction  $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$ . *J Appl Chem Biotechnol*, 23: 733-742.
- Bhatia, S. K., Perlmutter, D. D. (1983). Effect of the product layer on the kinetics of the CO<sub>2</sub>-lime reaction. *AIChE Journal*. 29: 79-86.
- Curran, G. P., Fink, C. E., Gorin, E. (1967). CO<sub>2</sub> acceptor gasification process. *Studies of acceptor properties. Adv. Chem. Ser.*, 69: 141-161.
- Deadman, A. J., Owens, A. J. (1962). Calcium cyanamide synthesis. Part 4-The reaction  $\text{CaO} + \text{CO}_2 = \text{CaCO}_3$ . *Trans. Faraday Soc.*, 58: 2027.

- Grasa, G. S., Abanades, J. C. (2006). CO<sub>2</sub> capture capacity of CaO in long series of carbonation/calcination cycles. *Industrial & Engineering Chemistry Research*, 45: 8846-8851.
- Grasa, G. S., Abanades, J. C., Alonso, M., Gonzalez, B. (2008). Reactivity of highly cycled particles of CaO in a carbonation/calcination loop. *Chemical Engineering Journal*, In Press, Corrected Proof.
- Kunii, D., Levenspiel, O. (1990). *Fluidization Engineering*. Butterworth-Heinemann
- Levenspiel, O. (2005). What Will Come after Petroleum?. *Industrial & Engineering Chemistry Research*, 44: 5073-5078.
- Mess, D., Sarofim, A. F., Longwell, J. P. (1999). Product Layer Diffusion during the Reaction of Calcium Oxide with Carbon Dioxide. *Energy & Fuels*, 13: 999-1005.
- Metz, B., Davidson, O., Coninck, H. d., Loos, M.Meyer, L. (2005 ). Special Report on Carbon Dioxide Capture and Storage. Intergovernmental Panel on Climate Change (IPCC). New York, NY (United States).
- Ochoa-Fernandez, E., Haugen, G., Zhao, T., Ronning, M., Aartun, I., Borresen, B., Rytter, E., Ronnekleiv, M.Chen, D. (2007). Process design simulation of H<sub>2</sub> production by sorption enhanced steam methane reforming: evaluation of potential CO<sub>2</sub> acceptors. *Green Chemistry*, 9: 654-662.
- Pfeifer, C., Puchner, B.Hofbauer, H. (2007). In-situ CO<sub>2</sub>-absorption in a dual fluidized bed biomass steam gasifier to produce a hydrogen rich syngas. *International Journal of Chemical Reactor Engineering*, 5.
- Rodriguez, N., Alonso, M., Grasa, G., Abanades, J. C. (2008). Heat requirements in a calciner of CaCO<sub>3</sub> integrated in a CO<sub>2</sub> capture system using CaO. *Chemical Engineering Journal*, 138: 148-154.

- Romeo, L. M., Abanades, J. C., Escosa, J. M., Paño, J., Giménez, A., Sánchez-Biezma, A., Ballesteros, J. C. (2008). Oxyfuel carbonation/calcination cycle for low cost CO<sub>2</sub> capture in existing power plants. *Energy Conversion and Management*, In Press, Corrected Proof , doi:10.1016/j.enconman.2008.03.022.
- Shimizu, T., Hiramata, T., Hosoda, H., Kitano, K., Inagaki, M., Tejima, K. (1999). A Twin Fluid-Bed Reactor for Removal of CO<sub>2</sub> from Combustion Processes. *Chemical Engineering Research and Design*, 77: 62-68.
- Sun, P., Grace, J. R., Lim, C. J., Anthony, E. J. (2007). The effect of CaO sintering on cyclic CO<sub>2</sub> capture in energy systems. *AIChE Journal*, 53: 2432-2442.
- Wang, J. S., Anthony, E. J., Abanades, J. C. (2004). Clean and efficient use of petroleum coke for combustion and power generation. *Fuel*, 83: 1341-1348.
- Weimer, T., Berger, R., Hawthorne, C., Abanades, J. C. (2008). Lime enhanced gasification of solid fuels: Examination of a process for simultaneous hydrogen production and CO<sub>2</sub> capture. *Fuel*, 87: 1678-1686.
- Yi, K. B., Harrison, D. P. (2005). Low-pressure sorption-enhanced hydrogen production. *Industrial & Engineering Chemistry Research*, 44: 1665-1669.

## Figure Captions

Figure 1: Scheme of the process for CO<sub>2</sub> capture using the lime carbonation-calcination loop.

Figure 2: Scheme of the kinetic model adopted to describe the progress of the carbonation reaction with time for different cycle numbers.

Figure 3: Sequence of calculations used to solve the proposed model.

Figure 4: Carbonation efficiency as a function of the solids inventory in the carbonator at different  $F_R/F_{CO_2}$  and (a)  $F_0/F_{CO_2}$  ratio of 0.1 and (b)  $F_0/F_{CO_2}$  ratio of 0.01.

Figure 5: Carbonation efficiency vs  $F_0/F_{CO_2}$  ratio at two different  $F_R/F_{CO_2}$  ratios and solids inventories.

Figure 6: CO<sub>2</sub> profiles along the carbonator for a solid inventory of 500 kg/MW and a  $F_0/F_{CO_2}$  ratio of 0.1 as a function of the  $F_R/F_{CO_2}$  ratio

Figure 7: Carbonation efficiency vs solid inventory as a function of the kinetic constant at a  $F_0/F_{CO_2}$  ratio of 0.1 and a  $F_R/F_{CO_2}$  ratio of 10.